

## CLAIMS

1. A process for cleaning a substance from a reactor surface, said process comprising:

5 providing a reactor containing the reactor surface, wherein: (a) the reactor surface is at least partially coated with a film of the substance; (b) the substance is at least one member selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate; and (c) the substance has a dielectric constant greater than the dielectric constant of silicon dioxide;

20 reacting the substance with a reactive agent to form a volatile product, wherein the reactive agent comprises at least one member selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and

25 removing the volatile product from the reactor to thereby remove the substance from the surface.

2. The process of claim 1, wherein the reactor is an atomic layer deposition reactor.

3. The process of claim 1, wherein the substance is at least one member selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfSi}_x\text{O}_y$ , and

$\text{ZrSi}_x\text{O}_y$  wherein  $x$  is a number greater than 0 and  $y$  is  $2x + 2$ , and any of the aforementioned compounds containing nitrogen.

- 5            4.        The process of claim 1, wherein the reactive agent is at least one member selected from the group consisting of  $\text{BCl}_3$ ,  $\text{COCl}_2$ ,  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{ClF}_3$ ,  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{NF}_z\text{Cl}_{3-z}$ , where  $z$  is an integer from 0 to 2.
- 10           5.        The process of claim 4, wherein the reactive agent is  $\text{COCl}_2$  formed by an in situ reaction of  $\text{CO}$  and  $\text{Cl}_2$ .
6.        The process of claim 4, wherein the reactive agent is  $\text{BCl}_3$ .
- 15           7.        The process of claim 1, wherein the reactive agent is a carbon-containing compound having the formula  $\text{C}_x\text{H}_y\text{Cl}_z$ , wherein  $x$  is a number ranging from 1 to 6,  $y$  is a number ranging from 0 to 13, and  $z$  is a number ranging from 1 to 14.
- 20           8.        The process of claim 1, wherein the reactive agent is conveyed to the substance from a gas cylinder, a safe delivery system or a vacuum delivery system.
9.        The process of claim 1, wherein the reactive agent is formed in situ by a point-of-use generator.
- 25           10.       The process of claim 1, wherein the substance is contacted with the reactive agent diluted with an inert gas diluent.
11.       The process of claim 1, wherein the reactive agent comprises a mixture of halogen-containing compounds.

12. The process of claim 11, where the mixture of halogen-containing compounds comprises at least one chlorine-containing gas and less than 50% by volume of at least one fluorine-containing gas.

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13. A process for removing a substance from at least a portion of the surface of a reaction chamber, the process comprising:

providing a reaction chamber wherein at least a portion of the surface is at least partially coated with the substance and wherein the substance has a dielectric constant of 4.1 or greater and is at least one member of the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer of the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate;

introducing a reactive agent into the reaction chamber wherein the reactive agent comprises at least one member selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound;

exposing the reactive agent to one or more energy sources sufficient to react the substance with the reactive agent and form a volatile product; and

removing the volatile product from the reaction chamber.

14. The process of claim 13, wherein the reactive agent is conveyed to the substance from a gas cylinder, a safe delivery system or a vacuum delivery system.
- 5 15. The process of claim 13, wherein the reactive agent is formed in situ by a point-of-use generator.
16. The process of claim 13, wherein the substance is contacted with the reactive agent diluted with an inert gas diluent.
- 10 17. The process of claim 13, wherein the reactive agent is deposited onto a nonreactive support.
- 15 18. The process of claim 13 wherein the reactive agent is exposed to one or more energy sources and the exposing step is conducted prior to the introducing step.
- 20 19. The process of claim 13, wherein the reactive agent is exposed to one or more energy sources and the exposing step is conducted during at least a portion of the introducing step.
20. The process of claim 13, wherein a temperature of the exposing step is at least 150 °C.
- 25 21. The process of claim 13, wherein a pressure of the exposing step is at least 10 mTorr.
22. The process of claim 13, wherein the reactive agent comprises a mixture of halogen-containing compounds.

23. The process of claim 13, where the mixture comprises at least one chlorine-containing gas and less than 50% by volume of at least one
- 5 24. An apparatus for removing a substance from at least one surface of a reactor, the apparatus comprising:
- 10 an at least one reactive agent selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and
- a non-reactive support having the at least one reactive agent deposited thereupon.
- 15 25. A mixture for removing a substance from at least one surface of a reactor, the mixture comprising:
- 20 an at least one reactive agent selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and
- an inert diluent.
- 25 26. A process for removing a substance from an at least one surface of a substrate, said process comprising:
- 30 providing the substrate wherein the substrate is at least partially coated with a film of the substance that is at least one member selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide other than  $\text{Al}_2\text{O}_3$ , a Group 13 metal

silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer of the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, or a nitrogen containing transition metal silicate; and wherein the substance has a dielectric constant greater than a dielectric constant of silicon dioxide;

reacting the substance with a reactive agent to form a volatile product, wherein the reactive agent comprises at least one member from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and

removing the volatile product from the substrate to thereby remove the substance from the substrate.

27. The process of claim 26, wherein the substance is at least one member selected from the group consisting of  $\text{HfO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfSi}_x\text{O}_y$ ,  $\text{ZrSi}_x\text{O}_y$ , where  $x$  is greater than 0 and  $y$  is  $2x + 2$ ,  $\text{Al}_2\text{Si}_w\text{O}_z$ , where  $w$  is greater than 0 and  $z$  is  $2w + 3$ , or any of the aforementioned compounds containing nitrogen.

28. The process of claim 26, wherein the substance is a laminate comprising layers of at least one material selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate.

29. The process of claim 26, wherein the reactive agent is at least one member selected from the group consisting of  $\text{BCl}_3$ ,  $\text{COCl}_2$ ,  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{ClF}_3$ ,  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{NF}_z\text{Cl}_{3-z}$ , where  $z$  is an integer from 0 to 2.
- 5 30. The process of claim 26, wherein the substance is at least one member selected from the group consisting of  $\text{HfO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfSi}_x\text{O}_y$ ,  $\text{ZrSi}_x\text{O}_y$ , where  $x$  is greater than 0 and  $y$  is  $2x + 2$ ,  $\text{Al}_2\text{Si}_w\text{O}_z$ , where  $w$  is greater than 0 and  $z$  is  $2w + 3$ , or any of the aforementioned compounds containing nitrogen.
- 10 31. A process for cleaning a substance from a reactor surface, said process comprising:
- 15 providing a reactor containing the reactor surface, wherein: (a) the reactor surface is at least partially coated with a film of the substance; (b) the substance is at least one member selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate; and (c) the substance has a dielectric constant greater than the dielectric constant of silicon dioxide;
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- 25 reacting the substance with a reactive agent comprising at least one fluorine-containing compound and at least one selected from a chlorine-containing compound, a bromine-containing compound, or an iodine-containing compound wherein the fluorine-containing compound is less than 50% by volume of an amount of the reactive agent; and
- 30 removing the volatile product from the reactor to thereby remove the substance from the surface.